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**Reactions of Thioketones Possessing a Conjugated C,C-Double Bond
with Diazo Compounds**

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The reactions of several thioketones containing a conjugated C,C-double bond with diazo compounds were investigated. All of the selected compounds reacted *via* a 1,3-dipolar cycloaddition with the C=S group and subsequent N₂-elimination to yield thiocarbonyl ylides as intermediates, which underwent a 1,3-dipolar electrocyclization to give the corresponding thiirane **25**, or, by a subsequent desulfurization, to give the olefins **33a**, **33b**. None of the intermediate thiocarbonyl ylides reacted *via* 1,5-dipolar electrocyclization. If the α,β -unsaturated thiocarbonyl compound bears an amino group in the β -position, the reactions with diazo compounds led to the 2,5-dihydrothiophenes **40a** – **40d**. In these cases, the proposed mechanism of the reactions led once more to the thiocarbonyl ylides **36** and thiiranes **38**, respectively. The thiiranes reacted *via* a S_Ni'-like mechanism to give the corresponding thiolate/ammonium-zwitterion **39**, which underwent a ring closure to yield the 2,5-dihydrothiophenes **40**. Also in these cases could no 1,5-dipolar electrocyclization be observed. The structures of several key products were established by X-ray crystallography.

1. Introduction. – The reactions of thiocarbonyl compounds **1** with diazo compounds **2** have been investigated extensively (*e.g.* [1-3], for reviews see [4][5]). The reactions proceed *via* a 1,3-dipolar cycloaddition to give the five membered 2,5-dihydro-1,3,4-thiadiazoles **3**, which, in general, at room temperature eliminate N₂ in a cycloreversion to give a thiocarbonyl ylide **4** (*Scheme 1*). In the absence of dipolarophiles, the thiocarbonyl ylides **4** react in a 1,3-dipolar electrocyclization to give the thiiranes **5**, which, either spontaneously or by treatment with Ph₃P, undergo a desulfurization to yield the olefins **6**. In the presence of appropriate dipolarophiles, *e.g.* an excess of the thiocarbonyl compound **1** [6][7], the thiocarbonyl ylides **4** can be intercepted to give 5-membered heterocycles of type **7** formed in a 1,3-dipolar cycloaddition (*Scheme 1*).

Scheme 1

In 1979, *Bak* and *Praefcke* have shown that the reaction of 1,2-diphenyl-2-thioxoethanone (**8**) with diphenyldiazomethane (**2a**) yields the corresponding 1,3-oxathiole **9**, which is formed by a 1,5-dipolar electrocyclization of the intermediate thiocarbonyl ylide **4a** under incorporation of the C=O bond [8] (*Scheme 2*). Analogous products have been obtained from thioketones and α -diazo carbonyl compounds [9 – 11].

Scheme 2

Recently, we have investigated reactions of diazo compounds with thiocarbonyl compounds containing a conjugated π -system, such as α -thioxoketones, α -thioxothioamides, etc. Since the reactions of **8**, *N,N*-dimethyl-2-phenyl-2-thioxothioacetamide (**9**), and *N*-[(dimethylamino)methylene]thiobenzamide (**10**) with different diazo compounds led to the five membered heterocycles **11**, **12** and **13**, respectively, usually in good yields [12][13] (*Scheme 3*), we decided to investigate

whether the analogous reaction takes place with α,β -unsaturated thioketones, *i.e.* when the conjugated π -system is a C,C-double bond.

Scheme 3

The synthesis of such α,β -conjugated thioketones proved to be no trivial task, because these products tend to dimerize in a [2 + 4]-cycloaddition. In a few cases it was possible to prepare the desired synthon and to react it with diphenyldiazomethane (**2a**). In order to make the thioketone less vulnerable to dimerization and to be able to carry out reactions with different diazo components, we extended the study to α,β -unsaturated thioketones with a β -amino substituent, *i.e.*, to vinylogous thioamides.

2. Results and Discussion. – 2.1. *Reaction with (Phenyl)(3,4-dihydro-2,4,6-triphenyl-2H-thiopyran-3-yl)methanethione (14).* It was attempted at first to synthesize the ‘D-dimer’ **15** of thiachalcone **16** by thionation of chalcone **17** [14]. The dimer would then be subjected to a retro-*Diels-Alder* reaction in the presence of diphenyldiazomethane (**2a**), which should lead to 2,3,5,5-tetraphenyl-2,3-dihydrothiophene (**18**) via 1,5-dipolar electrocyclization of the intermediate thiocarbonyl ylide with an extended π -system. Unfortunately, as reported by Li *et al.* [15], we were unable to reproduce the results of Saito *et al.* [14] and failed to isolate **15**. The only product obtained after thionation of **17** was the so-called ‘T-Dimer’ **14** [15]. Although **14** is less suitable as a precursor of **16** than **15**, we tried to carry out the reaction with **2a**. A reaction temperature of 50° to 60° and slow addition of the diazo compound to the solution of **14** in benzene were chosen as the reaction conditions to make a retro-*Diels-Alder* reaction possible. But **14** reacted with **2a** at the C=S group before the retro-*Diels-Alder* reaction took place and gave thiiran **19** (Scheme 4). The

structure of **19** was elucidated by an X-ray crystal-structure determination (*Fig. 1*). The asymmetric unit contains one molecule of **19** plus one half of a H₂O molecule disordered across two sites. The six-membered thiopyran ring shows a distorted envelope conformation with C(3) as the envelope flap and the phenyl substituents at C(4) and C(7) are almost coplanar. Surprisingly, **19** could not be desulfurized with Ph₃P to yield the corresponding alkene, most likely because the S-atom is too hindered for an attack of Ph₃P. *Fig.1* shows that the S-atom of the thiirane is indeed sheltered from a nucleophilic attack.

Scheme 4

Fig. 1

2.2. Reactions with γ -Oxo- α,β -unsaturated thioketones. As α,β -unsaturated thioketones are prone to dimerize via [2 + 4] cycloaddition, the preparation of these synthons needs special reaction conditions. One possibility is to create the thiocarbonyl group in the last step, *e.g.*, by a base catalyzed reaction at low temperature. The ethyl acetate **20** was synthesized according to a procedure described by *Mc Murry et al.* [17]. Silylation of **20** was achieved at room temperature by using NaI as a catalyst in an equimolar ratio to give the silylenolether **21**, which was converted into **23** by using sulfenylchloride **22** at -78° in CH₂Cl₂ (*Scheme 5*). The addition of **22** in the 2-position of silylenolethers of type **21** has never been observed in such reactions (see also the reaction of **30a,b** with **22**, *Scheme 7*). Then, the thioketone **24** was generated *in situ* by DBU-catalyzed elimination at low temperature and used immediately for the reaction with **2a**. After chromatographic work-up, thiiran **25** was obtained in 30% yield as a brownish oil.

Scheme 5

A mechanistic interpretation of the reaction is shown in *Scheme 6*. The reaction of **24** with **2a** led to the intermediate thiocarbonyl ylide **26** which could react to give stable products *via* three different pathways. Reactions a) and b), *i.e.* 1,5-dipolar electrocyclizations *via* the conjugated C=C or C=O bond, respectively, could yield either thiophene **27** or 1,3-oxathiole **28**. The third pathway c) would lead to thiirane **25** by a 1,3-dipolar electrocyclization. The spectroscopic data of the isolated product (IR: three intensive absorptions at 1741 (CO₂Et), 1714 (CO), and 1642 cm⁻¹ (C=C); ¹³C-NMR: 199.2 (CO), 167.3 (CO₂Et), 158.7 (*s*) and a *d* between 132.1 and 127.7 ppm (C=CH)) show clearly that it was neither the expected dihydrothiophene **27**, nor the 1,3-oxathiole **28**, but the thiirane **25**.

Scheme 6

Two other α,β -unsaturated thioketones **29a** and **29b** have been prepared as depicted in *Scheme 7*. In a Wittig-like reaction of cyclohex-2-enone (**30**) with benzaldehyde and pentanal, respectively, using the method of *Kozikowski and Jung* [18], the silylenolethers **31a** and **31b** were obtained. In the following steps, the protocol of *Capozzi et al.* was applied [19]. Treatment of **31** with **22** in THF at -78° gave the isoindole derivatives **32** in about 70% yield with a significant amount of the corresponding ketones of the hydrolyzed silylenolethers **31**. The crude products **32** in THF were treated with DBU at -78° to give the thioketones **29** by elimination of phthalimide. The crude **29a** and **29b**, respectively, were reacted with **2a** to give the alkenes **33a** and **33b** (*Scheme 7*). None of the expected intermediate thiiranes could be detected, but they spontaneously underwent desulfurization.

Scheme 7

Fig. 2

The structures of **33a** and **33b** have been established by X-ray crystallography (*Fig. 2*). Both structures are, with the exception of the substituent at C(7), quite similar. The conjugated π -system comprising O(1), C(1), C(2), C(3), C(7), and C(8) in **33a** or C(12) in **33b** is twisted about C(3)–C(7) (torsion angles C(2)–C(3)–C(7)–C(8) $131.5(3)^\circ$ and C(2)–C(3)–C(7)–C(12) $124.5(2)^\circ$, resp.). All phenyl substituents in compound **33a** are, because of steric reasons, twisted out of the plane formed by C(3), C(7) and C(8) (torsion angles C(7)–C(8)–C(21)–C(22) $126.6(3)^\circ$, C(7)–C(8)–C(15)–C(16) $-47.0(5)^\circ$, and C(8)–C(7)–C(9)–C(10) $134.2(3)^\circ$). The situation in **33b** is almost the same as in **33a**, with the exception of the butyl-substituent at C(7), which is in the expected staggered form.

The reactions of **2a** with the α,β -unsaturated thioketones **24**, **29a** and **29b** show that these conjugated thiocarbonyl compounds, which do not possess a heteroatom as part of the conjugated system, react readily with diazo compounds to give thiocarbonyl ylides as reactive intermediates. In contrast to thiocarbonyl ylides bearing conjugated C=O, C=S or C=N groups, these intermediates do not undergo a 1,5-dipolar electrocyclization. The products obtained, namely the alkenes **33a** and **33b** and the thiirane **25** are the result of a 1,3-electrocyclization.

2.3. Reactions with (E)-1-Phenyl-3-piperidinoprop-2-ene-1-thione (34) [20]. The α,β -unsaturated thioketone **34** reacted with **2a** much slower than with other thioketones [12][13]. Normally, the reactions between thioketones and diazo compounds are complete in a few min or h, while in the case of **34** the reactions needed several days at $40-80^\circ$. Nevertheless, the results were satisfactory as all spectra (MS, ^1H -, ^{13}C -NMR, IR) indicated the presence of dihydrothiophenes as the main products. In the

case of **2a**, the reaction had to be catalyzed by $\text{Rh}_2(\text{OAc})_4$. After 4 h at room temperature, a dihydro(triphenyl)(piperidino)thiophene was obtained in 50% yield. Analogous products were isolated in relatively good yields when **34** was treated with diazo compounds **2b**, **2c**, and diazocyclohexane (**2d**), respectively, under thermal conditions. In two cases, *i.e.* with **2b** and **2c**, we were able to grow single-crystals of the resulting products, and determine their crystal structures (*Fig. 3*). Surprisingly, the products were not the expected 4,5-dihydrothiophenes **37** which should be formed *via* 1,5-dipolar electrocyclization of the intermediate thiocarbonyl ylide **36**, but 2,5-dihydrothiophenes of type **40** (*Scheme 8*). Apparently, the S-atom is in a different position in the ring. A likely mechanistic explanation is given in *Scheme 8*: instead of the expected 1,5 dipolar electrocyclization of thiocarbonyl ylide **36** to give **37**, **36** reacted in a 1,3-dipolar electrocyclization to yield thiirane **38**. The latter underwent a ring opening in a S_{Ni}' -like reaction supported by the free electron pair of the N-atom to give the zwitterion **39**, which underwent a 5-exo-trig cyclization to give **40**.

Scheme 8

Whereas the reaction of **34** with **2c** yielded **40c** as the only product, the reaction with **2b** resulted in two diastereoisomeric products (*cis*-**40b** and *trans*-**40b**), which could be separated by MPLC. Recrystallization of the *cis*-isomer of **40b** and of **40c** gave crystals suitable for X-ray crystallography (*Fig. 3*). The data of the second isomer are in accordance with the estimated values for *trans*-**40b**'.

Fig. 3

3. Conclusion

The results in the present work show that it is possible to prepare the α,β -unsaturated thioketones **24**, **29a** and **29b** *in situ* by a base catalyzed reaction at low temperature. The products of their reactions with diphenyldiazomethane (**2a**) indicate that

thiocarbonyl ylides (*i.e.* **26**, *Scheme 6*) are formed as intermediates, which react in a 1,3-dipolar electrocyclization to give the corresponding thiiranes (*i.e.* **25**), but they do not undergo the expected 1,5-dipolar electrocyclization.

In the case of **34** with an amino group in β -position, diazo compounds **2a** – **2d** react also in a 1,3-dipolar cycloaddition onto the C=S group to give the 2,5-dihydro-1,3,4-thiadiazoles **35** as intermediates, followed by a spontaneous cycloreversion, which leads to the thiocarbonyl ylides **36**. A subsequent 1,3-dipolar electrocyclization yields the thiiranes **38**, which further rearrange to give finally the 2,5-dihydrothiophenes **40a** – **40d**. In all of the investigated reactions of α,β -unsaturated thioketones no 1,5-dipolar electrocyclization was observed.

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Experimental Part

1. *General*. See [12][13].

2. *Starting Materials*. All thiocarbonyl derivatives and their precursors and all diazo compounds were prepared following known protocols: (phenyl)(3,4-dihydro-2,4,6-triphenyl-2*H*-thiopyran-3-yl)methanethione (**14**) [14], diphenyldiazomethane (**2a**) [8], phenyldiazomethane (**2b**) [21], diazomethane (**2c**) [22], diazocyclohexane (**2d**) [23], ethyl(3-oxocyclohex-1-en-1-yl)acetate (**20**) [17], 1,3-dihydro-1,3-dioxo-2*H*-isoindole-2-sulphenylchloride (**22**) [24], (*E*)-1-phenyl-3-piperidinoprop-2-ene-1-thione (**34**) [20]. All other reagents are commercially available.

3. *General Procedure A (GP A)*: A stirred soln. of the precursor of the thiocarbonyl compound (2–6 mmol) in THF (50–100 ml) was cooled to -78° and DBU was added drop-wise by means of a syringe. The color of the soln. changed rapidly. After a few min, a purple soln. of **2a** in benzene (10–25 ml, 3–7 mmol) was added slowly and N_2 evolved. The color of the soln. changed again and the mixture was allowed to warm to r.t. The solvent was removed, and the crude product was purified by chromatography.

4. *General Procedure B (GP B)*: To a soln. of the thiocarbonyl compound (1–7 mmol) in CH_2Cl_2 (30–100 ml), the diazo compound (2–8 mmol) in toluene, Et_2O , THF or benzene (30–130 ml) was added by means of a dropping funnel, or, in the case of **2c**, by means of a *Pasteur* pipette. After total conversion of the thiocarbonyl compound, monitored either by TLC (treated for 20 s with a soln. of 1% Et_3N in Et_2O), color change or evolution of N_2 ²⁾, the solvent was evaporated and the mixture was purified by chromatography using silica gel, which had been treated with 3% Et_3N . Furthermore, the solvent was doped with 1% of Et_3N .

5. *Reaction of (Phenyl)(3,4-dihydro-2,4,6-triphenyl-2H-thiopyran-3-yl)methanethione (14) with 2a*. A soln. of **14** (2 mmol) in benzene (20 ml) was heated to 50° and **2a** (ca. 5 mmol) in benzene (10 ml) was added slowly. After total conversion of the starting material (TLC, changing of the color of the soln. from blue to yellow-brown), the solvent was evaporated, the crude product was purified by CC (hexane/AcOEt 10:1), and recrystallized from CH_2Cl_2 /hexane: 313 mg (51%) of 3,4-dihydro-2,4,6-triphenyl-3-(2,3,3-triphenylthiiran-2-yl)-2H-thiopyrane (**19**). Yellowish crystals. M.p. 137–

²⁾ The evolution of N_2 was determined volumetrically using a gas burette attached to the reaction vessel.

141°. IR: 3054 m , 3024 m , 2932 w , 1598 m , 1491 vs , 1444 s , 1267 w , 1235 w , 1180 w , 1156 w , 1077 w , 1031 m , 1001 w , 778 m , 751 vs , 696 vs . $^1\text{H-NMR}$: 7.75 (d , $J = 6.9$, 2 arom. H); 7.61 (d , $J = 6.9$, 2 arom. H); 7.56–6.45 (m , 26 arom. H); 6.12 (d , $J = 4.0$, =CH); 4.32 (d -like, H-C(2)); 3.71 (t -like, H-C(4)); 3.55 (br. s , H-C(3)). $^{13}\text{C-NMR}$: 142.0, 139.9, 139.8, 137.2 134.3, 133.4 (6 s , 6 arom. C); 132.0, 130.3, 128.5, 128.4, 128.1, 128.0, 127.8, 127.0, 126.7, 126.5, 126.1, 126.0, 125.9, 125.4 (14 d , 30 arom. CH); 120.3 (d , =CH); 65.3, 64.7 (2 s , 2 C(2'), C(3')); 52.3 (d , C(2)); 47.9 (d , C(4)); 39.4 (d , C(3)). CI-MS (*i*-butane): 391 (42, $[M + 1 - \text{C}_{15}\text{H}_{12}\text{S}]^+$), 358 (100, $[M - \text{C}_{15}\text{H}_{12}\text{S}_2]^+$), 225 (100, $[\text{C}_{15}\text{H}_{12}\text{S}]^+$). Anal. calc. for $\text{C}_{43}\text{H}_{34}\text{S}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$ (623.883): C 82.79, H 5.66, S 10.28; found: C 83.44, H 5.65, S 9.96.

Crystals suitable for an X-ray crystal-structure determination were grown from CH_2Cl_2 by slow evaporation of the solvent.

6. Reaction of Ethyl 2-(3-Oxocyclohexen-1-yl)-2-thioacetate (**24**) with **2a**.

6.1. Ethyl (*E/Z*)-2-{3-[(Trimethylsilyl)oxy]cyclohex-2-en-1-yliden}acetate (**21**). To a soln. of **20** (2 g, 10.98 mmol) and Me_3SiCl (1.63 g, 15 mmol) in DMF (15 ml), Et_3N (1.52 g, 15 mmol) was added slowly (10 min) whereby a white precipitate was formed. After a few min, NaI (1.8 g, 12 mmol) was added in one portion, and the mixture was stirred for 3 d at r.t. Pentane (30 ml) was added, and the resulting suspension was stirred for 1 h to give a more easily treatable precipitate. The soln. was filtered and the solvent was removed *in vacuo*. The residue was once more suspended in pentane (20 ml) and filtered to give **21** as a mixture of the (*E/Z*)-isomers: 2.54 g

(96%). Pale yellowish oil. $^1\text{H-NMR}$ (major product)³: 6.95 (*s*, HC(2)); 5.22 (*s*, HC(2')); 4.11–4.04 (*m*, CH₂O); 2.26–2.21 (*m*, H₂C(6')); 2.18–2.13 (*m*, H₂C(4')); 1.75–1.70 (*m*, H₂C(5')); 1.22–1.17 (*m*, MeCH₂); 0.24 (*s*, Me₃Si); (minor product): 5.38 (*s*, HC(2)); 5.34 (*s*, HC(2')); 0.18 (*s*, Me₃Si)⁴. $^{13}\text{C-NMR}$ (major product)³: 166.9 (*s*, CO₂); 163.4 (*s*, C(1')); 154.7 (*s*, C(3')); 109.6, 105.3 (*2d*, C(2), C(2')); 58.9 (*t*, CH₂O), 31.7 (*t*, C(6')); 30.8 (*t*, C(4')); 22.2 (*t*, C(5')); 14.3 (*q*, MeCH₂); 0.0 (*q*, (Me₃Si)); (minor product): 167.2 (*s*, CO₂); 162.5 (*s*, C(1')); 156.4 (*s*, C(3')); 107.5 (*d*, C(2) or C(2')); 58.9 (*t*, CH₂O), 30.5 (*t*, C(6')); 25.4 (*t*, C(4')); 22.0 (*t*, C(5')); 14.3 (*q*, MeCH₂); 0.1 (*q*, (Me₃Si)).

6.2. *Ethyl 2-[(1,3-Dihydro-1,3-dioxo-2H-isoindol-2-yl)sulfanyl]-2-(3-oxocyclohexen-1-yl)acetate (23)*. A soln. of **21** (0.50 g, 2.1 mmol) in dry CH₂Cl₂ (40ml) was cooled to –78°, and a soln. of **22** (0.47g, 2.2 mmol) in dry CH₂Cl₂ (*ca.* 20 ml) was added within 10 min by means of a syringe. The soln. was allowed to warm to r.t., the solvent was removed and the crude product was dried (h.v.) and analyzed without further purification: 0.69 g (100%) **23** (containing small amounts of **20**). $^1\text{H-NMR}$: 7.91–7.84 (*m*, 2 arom. H); 7.81–7.29 (*m*, 2 arom. H); 5.71 (*s*, HC(2')); 4.67 (*s*, HC(2)); 4.27 (*2q*, *J* = 7.1, CH₂O); 2.42–2.32 (*m*, H₂C(4'), H₂C(6')); 2.11–2.05 (*m*, H₂C(5')); 1.31 (*t*, *J* = 7.1, Me). $^{13}\text{C-NMR}$: 198.6 (*s*, C=O); 167.5 (*s*, N(CO)₂); 166.3 (*s*, =C(1')); 155.3 (*s*, CO₂Et); 134.9, 124.0 (*2d*, 4 arom. CH); 131.5 (*s*, 2 arom. C);

³) It was not possible to assign the spectra to (*E*)- and (*Z*)-**21** on the basis of the available information. Due to thermodynamic stability, we expect that the minor product is the (*Z*)-isomer.

⁴) Other signals overlap with the corresponding signals of the major product.

130.0 (*d*, C(2')); 62.7 (*t*, CH₂O); 59.5 (*d*, C(2)); 37.1 (*t*, H₂C(4')); 25.4 (*t*, H₂C(6')); 22.2 (*t*, H₂C(5')); 13.9 (*q*, Me).

6.3. Ethyl 2-(3-Oxocyclohexen-1-yl)-3,3-diphenylthiirane-2-carboxylate (**25**).

According to *GP A*, a soln. of **23** (3.1 mmol) in CH₂Cl₂ (30 ml) was treated with a catalytic amount of DBU. After 30 min, an excess of **2a** (*ca.* 5 mmol) dissolved in benzene (20 ml) was added drop-wise. The mixture was diluted with 40 ml of CH₂Cl₂ and extracted with cold, sat. *aq.* NH₄Cl. The org. layer was dried (Na₂SO₄) and the solvent removed. CC (CH₂Cl₂/Et₂O 200:1): 344 mg (30%) of **25**. Brownish oil. IR: 3058_w, 3027_w, 2942_m, 1741_{vs}, 1714_{vs}, 1642_{vs}, 1623_m, 1491_m, 1445_s, 1341_m, 1324_m, 1298_m, 1241_{vs}, 1187_s, 1135_m, 1094_m, 1018_m, 974_w, 754_m, 703_{vs}. ¹H-NMR: 7.50–7.18 (*m*, 10 arom. H); 6.30 (*s*, =CH); 3.95–3.83 (*m*, CH₂O); 2.58 (*ddd*, *J* = 17.8, 2.7, 1.7, 1 H of H₂C(6')); 2.30–2.10 (*m*, H₂C(4')); 1.97 (*ddd*, *J* = 17.8, 4.3, 0.9, 1 H of H₂C(6')); 1.76–1.65, 1.31–1.19 (2*m*, H₂C(5')); 0.91 (*t*, *J* = 7.1, Me). ¹³C-NMR: 199.2 (*s*, CO); 167.3 (*s*, CO₂Et); 158.7 (*s*, C(1')); 139.5, 137.4 (2*s*, 2 arom. C); 132.1, 129.8, 129.6, 127.9, 127.8, 127.8, 127.7 (7*d*, 10 arom. C, =CH); 77.3 (*s*, C(3)); 62.7 (*s*, C(2)); 62.3 (*t*, CH₂O); 37.3 (*t*, C(4')); 30.7 (*t*, C(6')); 22.7 (*t*, C(5')); 13.5 (*q*, Me). CI-MS: 396 (5, [*M* + NH₄]⁺), 379 (54, [*M* + 1]⁺), 364 (5), 347 (100, [*M* + 1 – S]⁺).

7. Reactions of (3-Oxocyclohexen-1-yl)(phenyl)methanethione (**29a**) and 1-(3-Oxocyclohexene-1-yl)pentanethione (**29b**) with **2a**.

7.1. (E/Z)-3-{3-[Trimethylsilyl]oxy}cyclohex-2-en-1-ylidene}methyl)benzene (**31a**). To a cold (0°) soln. of cyclohex-2-enone (**30**) (2.06 g, 21.44 mmol) and Ph₃P (5.62 g, 21.44 mmol) in dry THF (50 ml), TMSOTf (4.15 ml, 21.44 mmol) was added slowly. The mixture was cooled to –78°, and a soln. of BuLi (2.5 M in hexane, 8.4 ml, 21.44 mmol) was added slowly whereby the soln. changed to a dark brown suspension.

Then, benzaldehyde (2.17 ml, 21.44 mmol) was added whereupon the color turned to pale-orange. The solvent was removed and the residue was purified by “kugelrohr”-distillation (115°, 5 mbar): 3.53 g (64%) of almost pure **31a**. Colorless oil. ¹H-NMR: 7.12–7.02, 6.97–6.93 (2*m*, 5 arom. H); 5.88, 5.82, 5.81, 5.37 (4*s*, HC(2), PhCH)⁵; 2.38–2.33, 2.17–2.12 (2*m*, H₂C(4)); 2.04–1.97 (*m*, H₂C(6)); 1.66–1.61, 1.57–1.52 (2*m*, H₂C(5)); 0.01 (*s*, Me₃Si). GC-MS (EI): 258 (100, *M*⁺).

7.2. (*E/Z*)-3-Pentylidene-1-[(trimethylsilyl)oxy]cyclohexene (**31b**). To a cold (0°) soln. of cyclohex-2-enone (**30**) (1.92 g, 20 mmol) and Ph₃P (5.25 g, 20 mmol) in dry THF (60 ml), TMSOTf (4.76 g, 20 mmol) was added slowly. The soln. was cooled to –78°, and a soln. of BuLi (1.6 M in hexane, 13 ml, 20 mmol) was added slowly whereby the soln. changed to a dark brown suspension. Then, pentanal (1.72 ml, 20 mmol) was added by means of a syringe, and the color turned to orange. A part of the solvent was removed and the suspension was filtered. Then, the solvent was removed completely and the residue was purified by “kugelrohr”-distillation (80–120°, 0.2 mbar): 1.53 g (32%) of almost pure **31b**. Colorless oil. ¹H-NMR: 5.32 (*s*, HC(2)); 4.95 (*t*-like, HC(1’)); 2.17–2.13 (*m*, H₂C(6)); 2.12–2.10 (*m*, H₂C(4)); 2.05–1.97 (*m*, H₂C(2’)); 1.70–1.63 (*m*, H₂C(5)); 1.29–1.24 (*m*, H₂C(3’), H₂C(4’)); 0.85–0.80 (*m*, Me); 0.14 (*s*, Me₃Si). ¹³C-NMR: 153.9 (*s*, C(1)); 134.2 (*s*, C(3)); 122.2 (*d*, C(2)); 110.4 (*d*, C(1’)); 31.8 (*t*, C(6)); 30.2 (*t*, C(4)); 27.0 (*t*, C(2’)); 24.1 (*t*, C(5)); 22.3 (*t*, C(3’)); 22.0 (*t*, C(4’)); 13.6 (*q*, C(5’)); 0.0 (*q*, Me₃Si).

⁵) The product is a mixture of two stereoisomers (*E/Z*), therefore, four signals for the two olefinic H-atoms are to be expected. The assignment of the signals to HC(2) and PhCH is not clear.

7.3. 2-[[*(3-Oxocyclohexen-1-yl)(phenyl)methyl*]*sulfanyl*]-1*H*-isoindole-1,3-(2*H*)-dione (**32a**). A soln. of **31a** (1.01 g, 3.90 mmol) in dry THF (40 ml) was cooled to –78° and a soln. of **22** (0.71 g, 3.90 mmol) in dry THF (*ca.* 25 ml) was added by means of a dropping funnel (30 min). The soln. was allowed to warm to r.t., the solvent was removed, and the crude product was dried (h.v.) and analyzed without further purification: 1.27 g (89%) of **32a**⁶. Yellowish plates. IR: 2954*s*, 2871*m*, 1784*s*, 1738*vs*, 1704*vs*, 1666*vs*, 1495*m*, 1454*m*, 1340*m*, 1279*vs*, 1037*vs*, 968*m*, 866*s*, 763*m*, 710*vs*. ¹H-NMR: 7.87–7.76 (*AA'**BB'*, 2 arom. H); 7.74–7.66 (*AA'**BB'*, 2 arom. H); 7.38–7.14 (*m*, 4 arom. H); 7.10–7.07 (*m*, 1 arom. H); 5.80 (*t*, *J* = 1.3⁷), *H*CPh); 5.18 (*s*, HC(2')); 2.31–2.06 (*m*, H₂C(4'), H₂C(6')); 1.92–1.75 (*m*, H₂C(5')). ¹³C-NMR: 199.1 (*s*, CO); 167.6 (*s*, N(CO)₂); 160.6 (*s*, =C); 136.9 (*d*, 1 arom. C); 134.7, 123.8 (2*d*, 4 arom. CH); 131.5 (*s*, 2 arom. C); 129.0, 128.9, 128.7, 128.3 (4*d*, 5 arom. CH, C(2')); 60.7 (*d*, CHPh); 37.2 (*t*, H₂C(4')); 29.1 (*t*, H₂C(6')); 25.8 (*t*, H₂C(5')). GC-MS (EI): 220 (30), 205 (100), 177 (30), 133 (15).

7.4. 2-[[*(1-Oxocyclohexen-1-yl)pentyl*]*sulfanyl*]-1*H*-isoindole-1,3(2*H*)-dione (**32b**). A soln. of **31b** (1.44 g, 6 mmol) in dry THF (100 ml) was cooled to –78° and a soln. of **22** (1.28 g, 6 mmol) in dry THF (*ca.* 40 ml) was added by means of a dropping funnel (30 min). The soln. was allowed to warm to r.t., the solvent was then removed, and the crude product was dried (h.v.) and analyzed without further purification: 1.97 g (92%) of **32b**. Yellowish oil. ¹H-NMR: 7.90–7.83, 7.79–7.71 (2*m*, 4 arom. H); 5.54 (*s*,

⁶) The NMR- and MS-spectra indicated a large amount of side product, which was formed by hydrolysis of **31a**.

⁷) The coupling constant of 1.3 Hz is also observed in one pair of signals in the *m* of H₂C(6).

HC(2')); 3.84–3.72 (*dd*, $J = 6.4, 6.2$, HC(1'')); 2.40–2.29 (*m*, H₂C(4')); 2.09–1.98 (*m*, H₂C(6')); 1.76–1.60 (*m*, H₂C(5')); 1.50–1.29 (*m*, H₂C(2''), H₂C(3''), H₂C(4'')); 0.94–0.90 (*m*, Me). ¹³C-NMR: 199.2 (*s*, CO); 167.9 (*s*, N(CO)₂); 161.7 (*s*, =C); 134.7, 123.8 (*d*, 4 arom. CH); 131.5 (*s*, 2 arom. C); 128.1 (*d*, C(2')); 57.6 (*d*, HC(1'')); 37.4 (*t*, H₂C(4')); 29.4 (*t*, H₂C(6')); 27.9 (*t*, H₂C(5')); 24.4 (*t*, H₂C(2'')); 22.2 (*t*, H₂C(3''), H₂C(4'')); 13.7 (*q*, Me).

7.5. 3-(1,2,2-Triphenylvinyl)cyclohex-2-en-1-one (**33a**). According to *GP A*, a soln. of **32a** (1.35 mmol) in THF (60 ml) was treated with a catalytic amount of DBU. Then, an excess of **2a** dissolved in benzene was added drop-wise. CC (hexane/AcOEt 10:1 to 1:1) yielded 200 mg (42%) of **33a**. Colorless crystals. M.p. 179–181°. IR: 3077*m*, 3053*m*, 3026*m*, 2947*m*, 2920*m*, 2878*m*, 2864*m*, 1651*vs*, 1597*s*, 1490*s*, 1454*m*, 1443*s*, 1410*m*, 1360*m*, 1344*s*, 1323*m*, 1306*m*, 1296*m*, 1253*m*, 1240*s*, 1193*m*, 1183*m*, 1154*m*, 1132*m*, 1075*m*, 884*m*, 773*s*, 762*m*, 751*m*, 726*m*, 699*vs*. ¹H-NMR: 7.22–6.85 (*m*, 15 arom. H); 5.76 (*t*, $J = 1.4$, CH); 2.24–2.14 (*m*, H₂C(6), H₂C(4)); 1.81–1.73 (*m*, H₂C(5)). ¹³C-NMR: 199.4 (*s*, CO); 165.4 (*s*, C(3)); 142.9, 142.5, 142.0, 140.6 (4*s*, 3 arom. C, 2 =C)⁸; 131.2, 131.1, 130.3, 129.8, 128.1, 127.7, 127.6, 127.0, 126.9 (9*d*, 15 arom. CH, =CH); 37.3 (*t*, C(6)); 30.5 (*t*, C(4)); 23.1 (*t*, C(5)). ESI-MS: 350 (100, *M*⁺), 273 (58, [*M* – Ph]⁺), 215 (18), 165 (17).

Crystals suitable for an X-ray crystal-structure determination were grown from CH₂Cl₂/hexane by slow evaporation of the solvent.

7.6. 3-(1,1-Diphenylhex-1-en-2-yl)cyclohex-2-en-1-one (**33b**). According to *GP A*, a soln. of **32b** (6 mmol) in THF (60 ml) was treated with DBU (6 mmol). Then, an

⁸) The signals of two of the three arom. C-atoms overlap.

excess of **2a** dissolved in benzene was added drop-wise. CC (hexane/Et₂O 2:1 to 1:3) gave 480 mg (25%) of **33b**. Colorless crystals. M.p. 115–116°. IR: 2949_s, 2923_m, 2891_m, 2865_m, 2858_m, 2844_m, 1671_{vs}, 1606_s, 1582_m, 1492_m, 1446_m, 1413_w, 1375_w, 1343_m, 1322_m, 1293_m, 1254_s, 1235_m, 1186_m, 1163_w, 1127_m, 1101_m, 1077_m, 1029_m, 884_m, 774_m, 768_s. ¹H-NMR: 7.37–7.07 (*m*, 10 arom. H); 6.00 (*s*, =CH); 2.31–2.25 (*m*, H₂C(6), CH₂(Bu)); 2.17–2.13 (*m*, H₂C(4)); 1.82–1.74 (*m*, H₂C(5)); 1.46–1.36, 1.32–1.20 (2*m*, 2 CH₂(Bu)); 0.84 (*t*, *J* = 7.3, Me). ¹³C-NMR: 199.4 (*s*, CO); 166.0 (*s*, C(3)); 142.4, 142.0, 140.4, 140.1 (4*s*, 2 arom. C, 2 =C); 129.4, 129.2, 129.1, 128.0, 127.8, 127.1, 127.0 (7*d*, 10 arom. CH, =CH); 37.3 (*t*, C(6)); 34.4 (*t*, C(4)); 30.9, 30.7 (2*t*, C(5), CH₂(Bu)); 23.0, 22.7 (2*t*, 2 CH₂(Bu)); 13.7 (*q*, Me). CI-MS: 331 (100, [*M* + 1]⁺). Anal. calc. for C₂₄H₂₆O (330.470): C 87.23, H 7.93; found: C 87.05, H 7.97.

Crystals suitable for an X-ray crystal-structure determination were grown from CH₂Cl₂/hexane by slow evaporation of the solvent.

8. Reaction of (E)-1-Phenyl-3-piperidinoprop-2-ene-1-thione (**34**).

8.1. 1-(2,5-Dihydro-4,5,5-triphenylthiophen-2-yl)piperidine (**40a**). According to *GP B*, **34** (1.86 mmol) in CH₂Cl₂ (40 ml) and **2a** (*ca.* 2.5 mmol) in benzene (*ca.* 40 ml) were used. To the soln., a catalytic amount (10 mg) of Rh₂(OAc)₄ was added and the mixture was stirred for 4 h. The crude product was purified by CC (CH₂Cl₂/Et₂O 400:1): 365 mg (*ca.* 50%) of **40a**. Yellowish crystals. M.p. 130–133°. IR: 3055_m, 3029_m, 2931_{vs}, 2852_s, 2804_m, 1633_w, 1597_m, 1575_m, 1493_s, 1465_m, 1442_s, 1385_w, 1365_m, 1335_s, 1323_m, 1308_m, 1266_w, 1237_m, 1221_m, 1182_w, 1155_m, 1115_s, 1098_{vs}, 1034_m, 981_s, 895_m, 861_m, 774_s, 763_{vs}, 736_{vs}, 697_{vs}. ¹H-NMR⁹): 7.75–6.97 (*m*, 15

⁹) The spectra are not clean because of fast decomposition of the substance.

arom. H); 6.19 (*d*, $J = 2.9$, HC(3')); 4.65 (*d*, $J = 2.9$, HC(2')); 2.43 (br. *s*, 2 CH₂N); 1.12 (br. *s*, 2 CH₂); 0.97 (br. *s*, CH₂). ¹³C-NMR ((D₆)DMSO): 149.2, 144.5, 141.5, 139.8 (4*s*, 3 arom. C, C(4')); 133.1, 132.6, 129.5, 129.4, 128.6, 128.5, 128.3, 128.0, 127.8, 127.5, 127.1, 127.0, 126.8, 126.3, 126.1 (15*d*, 15 arom. CH); 117.0 (*d*, C(3')); 78.8 (*d*, C(2')); 71.4 (*s*, C(5')); 50.2 (*t*, 2 CH₂N); 25.9 (*t*, 2 CH₂); 23.8 (*t*, CH₂). CI-MS (NH₃): 398 (10, [*M* + 1]⁺), 361 (10), 348 (30), 313 (100, [*M* + 1 – piperidine]⁺), 299 (6), 86 (9).

8.2. *cis*-1-(2,5-Dihydro-4,5-diphenylthiophen-2-yl)piperidine (*cis*-**40b**) and *trans*-1-(2,5-Dihydro-4,5-diphenylthiophen-2-yl)piperidine (*trans*-**40b**). According to GP B, **34** (1.2 mmol) in toluene (10 ml) and **2b** (*ca.* 4 mmol) in toluene (*ca.* 50 ml) were used. The soln. was stirred at 80° for 4 d. After total conversion of the starting material (TLC), the soln. was cooled to r.t., the solvent was removed *in vacuo*, and the crude product was purified by CC (hexane/AcOEt 10:1 + 3% NEt₃): 181 mg (49%) of a mixture of *cis*-**40b** and *trans*-**40b**, which was separated by MPLC (hexane/AcOEt 20:1 + 2% Et₃N) to give 60 mg (16%) of *cis*-**40b** and 50 mg (14%) of *trans*-**40b**.

Data of *cis*-**40b**: Oily, yellowish crystalline. Mp. 106–123°. IR (Golden Gate ATR): 2934_w, 2849_w, 2810_w, 1644_w, 1601_w, 1574_w, 1495_w, 1454_w, 1439_w, 1392_w, 1368_w, 1338_w, 1309_w, 1245_w, 1222_w, 1149_w, 1100_m, 1076_w, 1036_w, 977_w, 911_w, 860_w, 846_w, 773_w, 759_m, 724_m, 698_s, 688_m. ¹H-NMR: 7.38–7.09 (*m*, 10 arom. H); 6.37 (*dd*, $J = 2.4, 2.0$, HC(3')); 5.92 (*dd*, $J = 2.4, 2.0$, HC(5')); 5.73 (*t*-like, $J = 2.0$, HC(2')); 2.56 (*t*-like, 2 CH₂N); 1.71–1.51 (*m*, 2 CH₂); 1.50–1.38 (*m*, CH₂). ¹³C-NMR: 144.6, 143.0, 134.9 (3*s*, C(4'), 2 arom. C); 129.6, 128.7, 128.5, 128.3, 127.7, 127.0, 126.7 (7*d*, 10 arom. CH, C(3')); 83.3 (*d*, C(2')); 55.7 (*d*, C(5')); 50.2 (*t*, 2 CH₂N); 26.2 (*t*, 2 CH₂); 23.9 (*t*, CH₂). CI-MS (NH₃): 291 (24), 290 (100, [*M* – S + 1]⁺). Anal. calc.

for C₂₁H₂₅NS (321.16): C 78.46, H 7.21, N 4.36, S 9.97; found: C 78.13, H 6.82, N 4.29 S 9.54.

Crystals suitable for an X-ray crystal-structure determination were grown from Et₂O/hexane by slow evaporation of the solvent.

Data of *trans*-**40b**: Pale yellowish oily crystals. M.p. 110–138°. IR (Golden Gate ATR): 2933_w, 2877_w, 2851_w, 2798_w, 1575_w, 1496_w, 1446_m, 1363_w, 1331_w, 1208_w, 1149_w, 1092_m, 1034_w, 977_m, 850_w, 820_w, 768_m, 754_m, 726_m, 714_m, 693_m. ¹H-NMR: 7.33–7.07 (*m*, 10 arom. H); 6.31 (*dd*, *J* ≈ 2.5, 1.9, HC(3′)); 5.99 (*dd*, *J* = 5.1, 2.5, HC(5′)); 5.68 (*dd*, *J* = 5.1, 1.9, HC(2′)); 2.63–2.47 (*m*, 2 CH₂N); 1.71–1.52 (*m*, CH₂); 1.49–1.42 (*m*, CH₂). ¹³C-NMR: 145.9 (*s*, C(4′)); 142.6, 134.7 (2*s*, 2 arom. C); 129.5, 128.5, 128.2, 127.7, 127.6, 126.9 (6*d*, 10 arom. CH, C(3)); 83.3 (*d*, C(2′)); 57.3 (*d*, C(5′)); 49.7 (*t*, 2 CH₂N); 25.6 (*t*, 2 CH₂); 24.2 (*t*, CH₂). CI-MS (NH₃): 291 (24), 290 (100, [*M* – S + 1]⁺).

8.3. *1-(2,5-Dihydro-4-phenylthiophen-2-yl)piperidine (40c)*. According to GP B, **34** (1.3 mmol) in CH₂Cl₂ (20 ml) and **2c** (*ca.* 6 mmol) in THF (30 ml) were used. The crude product was purified by CC (hexane/AcOEt 2:1): 174 mg (55%) of **40c**. Yellowish oily crystals. M.p. not measurable. IR: 2932_{vs}, 2852_s, 2816_s, 2788_s, 2748_m, 1639_w, 1598_w, 1575_w, 1496_s, 1468_m, 1450_s, 1441_s, 1429_m, 1384_m, 1365_s, 1335_s, 1321_s, 1304_s, 1282_w, 1263_w, 1247_m, 1232_s, 1213_s, 1152_s, 1128_m, 1116_s, 1099_{vs}, 1075_m, 1036_m, 994_s, 975_s, 964_m, 921_m, 863_s, 847_s, 776_s, 758_{vs}, 748_{vs}, 713_{vs}, 687_{vs}, 636_m. ¹H-NMR (CDCl₃): 7.39–7.18 (*m*, 5 arom. H); 6.14 (*q*-like, =CH); 5.72 (*q*-like, HC(2′)); 3.93 (*q*-like, H₂C(5′)); 2.50–2.36 (*m*, 2 CH₂N); 1.57–1.36 (*m*, 3 CH₂). ¹³C-NMR: 142.2 (*s*, C(4′)); 134.3 (*s*, 1 arom. C); 127.6, 127.2, 125.1 (3*d*, 5 arom. CH); 125.0 (*d*, C(3′)); 83.4 (*d*, C(2′)); 48.6 (*t*, C(5′)); 36.8 (*t*, 2 CH₂N); 24.7,

23.3 (2*t*, 3 CH₂). CI-MS (NH₃): 246 (100, [*M* + 1]⁺), 214 (86, [*M* + 1 – S]⁺), 86 (27, [piperidine + 1]⁺).

Crystals suitable for an X-ray crystal-structure determination were grown from Et₂O/hexane by slow evaporation of the solvent.

8.4. *1-(4-Phenyl-1-thiaspiro[4.5]dec-3-en-2-yl)piperidine* (**40d**). According to *GP B*, **34** (1.3 mmol) in CH₂Cl₂ (10 ml) and **2d** (*ca.* 4 mmol) in CH₂Cl₂ (*ca.* 50 ml) were used. To the soln. a catalytic amount (5 mg) of Rh₂(OAc)₄ was added, and the mixture was stirred at r.t. for 7 h. Then, the solvent was removed *i.v.* and the crude product was purified by CC (hexane/AcOEt 2:1): 364 mg (92%) of **40d**. Yellowish crystals. M.p. 130–133°. IR: 2933_{vs}, 2853_{vs}, 2752_w, 1662_w, 1574_w, 1494_m, 1441_{vs}, 1363_m, 1333_s, 1322_m, 1302_m, 1262_m, 1249_m, 1222_m, 1205_m, 1157_m, 1116_s, 1097_{vs}, 1072_m, 1033_m, 984_{vs}, 967_w, 904_m, 867_m, 766_{vs}, 719_m, 698_{vs}. ¹H-NMR: 7.33–7.22 (*m*, 3 arom. H); 7.13–7.07 (*m*, 2 arom. H); 5.56 (*d*, *J* = 2.4, =CH); 5.45 (*d*, *J* = 2.4, HC(3')); 2.52–2.39 (*m*, 2 CH₂N); 1.79–1.38 (*m*, 8 CH₂). ¹³C-NMR: 153.0 (*s*, 1 arom. C); 137.0 (*s*, C(4')) 129.1, 128.0, 127.6, 127.2 (4*d*, 5 arom. CH, C(3')); 79.9 (*d*, C(2')); 66.4 (*s*, C(5')); 49.9 (br. *t*, 2 CH₂N); 39.3, 37.6 (2*t*, 2 CH₂); 25.7, 25.0, 24.8, 24.2, 23.9 (5*t*, 6 CH₂). EI-MS: 313 (35, *M*⁺), 280 (10, [*M* – S – 1]⁺), 229 (95, [*M* – C₅H₁₀N]⁺), 199 (40), 99 (100), 98 (91), 81 (54), 69 (24), 55 (46), 43 (66).

9. *X-Ray Crystal-Structure Determination of 19, 33a, 33b, cis-40b and 40c* (Table and Figs. 1–3)¹⁰). All measurements were performed on a *Nonius KappaCCD*

¹⁰) CCDC-616929–616933 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Center* via http://www.ccdc.cam.ac.uk/data_request/cif.

diffractometer [25] using graphite-monochromated $\text{MoK}\alpha$ radiation (λ 0.71073 Å) and an *Oxford Cryosystems Cryostream* 700 cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in *Figs. 1-3*. Data reduction was performed with *HKL Denzo* and *Scalepack* [26]. The intensities were corrected for *Lorentz* and polarization effects, and with the exceptions of **33a** and **33b**, absorption corrections based on the multi-scan method [27] were applied. Equivalent reflections were merged. The structures were solved by direct methods using SIR92 [28] which revealed the positions of all non-H-atoms. In the case of **19**, the asymmetric unit contains one molecule of the heterocyclic compound plus two disordered sites for a H_2O molecule, each of which is one quarter occupied, thus giving one half of a H_2O molecule in the asymmetric unit. For all structures, the non-H-atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me group in **33b**). The refinement of each structure was carried out on F^2 using full-matrix least-squares procedures, which minimized the function $\sum w(F_o^2 - F_c^2)^2$. Corrections for secondary extinction were applied, except in the case of **19**. For **19**, **33a**, **33b**, *cis*-**40b**, and **40c**, 5, 1, 3, 1 and 1 reflections, respectively, whose intensities were considered as extreme outliers, were omitted from the final refinement. Compounds **33a** and **33b** crystallize in non-centrosymmetric space groups. In each case, the absolute direction of the polar axis was chosen arbitrarily. Neutral atom scattering factors for non-H-atoms were taken from [29a], and the scattering factors for H-atoms were taken from [30]. Anomalous dispersion effects were included in F_c [31]; the values for f' and f'' were those of [29b]. The values of the mass attenuation coefficients are those of [29c]. All calculations were performed using the SHELXL97 [32] program.

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Legends

Fig. 1. *ORTEP Plot* [16] of the molecular structure of **19** (50% probability ellipsoids, arbitrary numbering of the atoms, the H₂O molecules omitted for clarity)

Fig. 2. *ORTEP Plots* [16] of the molecular structures of a) **33a** and b) **33b** (50% probability ellipsoids, arbitrary numbering of the atoms)

Fig. 3. *ORTEP Plots* [16] of the molecular structures of a) *cis*-**40b** and b) **40c** (50% probability ellipsoids, arbitrary numbering of the atoms)

Table. *Crystallographic Data of Compounds 19, 33a, 33b, cis-40b and 40c*

	19	33a	33b
Crystallized from	CH ₂ Cl ₂	CH ₂ Cl ₂ /hexane,	CH ₂ Cl ₂ /hexane
Empirical formula	C ₄₃ H ₃₄ S ₂ ·0.5H ₂ O	C ₂₆ H ₂₂ O	C ₂₄ H ₂₆ O
Formula weight [g mol ⁻¹]	623.87	350.46	330.47
Crystal color, habit	colorless, prism	yellow, prism	colorless, prism
Crystal dimensions [mm]	0.12 × 0.22 × 0.30	0.17 × 0.22 × 0.27	0.25 × 0.30 × 0.30
Temperature [K]	160(1)	160(1)	160(1)
Crystal system	triclinic	Monoclinic	orthorhombic
Space group	<i>P</i> ⁻ ₁	<i>P</i> 2 ₁	<i>Pca</i> 2 ₁
<i>Z</i>	2	2	4
Reflections for cell determination	32416	1806	2521
2 θ range for cell determination [°]	4–60	4–50	4–55
Unit cell parameters <i>a</i> [Å]	9.7018(2)	9.9821(5)	22.0889(5)
<i>b</i> [Å]	13.0899(3)	9.4828(4)	9.7500(2)
<i>c</i> [Å]	13.9694(2)	10.7165(5)	8.8389(2)
α [°]	85.716(1)	90	90
β [°]	83.236(1)	107.853(2)	90
γ [°]	75.462(1)	90	90
<i>V</i> [Å ³]	1703.41(6)	965.56(8)	1903.61(7)
<i>D_x</i> [g cm ⁻³]	1.216	1.205	1.153
μ (MoK α) [mm ⁻¹]	0.187	0.0714	0.0682
Scan type	ϕ and ω	ω	ϕ and ω
2 θ (max) [°]	60	50	55
Transmission factors (min; max)	0.867; 0.982	-	-
Total reflections measured	46930	12782	26913
Symmetry independent reflections	9964	1803	2328
Reflections with <i>I</i> > 2 σ (<i>I</i>)	7526	1634	1915
Reflections used in refinement	9959	1802	2325
Parameters refined	424	245	228
Final <i>R</i> (<i>F</i>) [<i>I</i> > 2 σ (<i>I</i>) reflections]	0.0465	0.0448	0.0424
<i>wR</i> (<i>F</i> ²) (all data)	0.1271	0.1178	0.1063
Weighting parameters (a; b) ^a :	0.0582; 0.6749	0.0639; 0.2654	0.0552; 0.1724
Secondary extinction coeff.	-	0.05(1)	0.026(4)
Goodness of fit	1.018	1.054	1.057
Final Δ_{\max}/σ	0.001	0.001	0.001
$\Delta\rho$ (max; min) [e Å ⁻³]	0.53; -0.32	0.28; -0.18	0.19; -0.15
^a) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$			

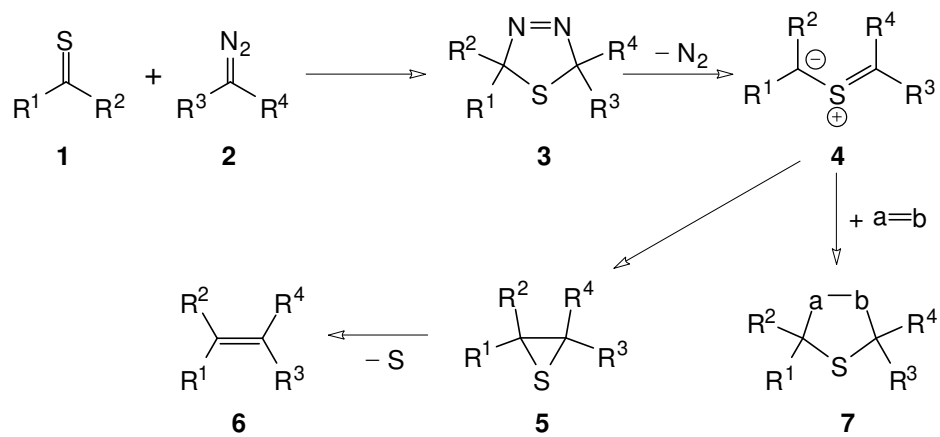
Table. *Crystallographic Data of Compounds 19, 33a, 33b, cis-40b and 40c*

(continued)

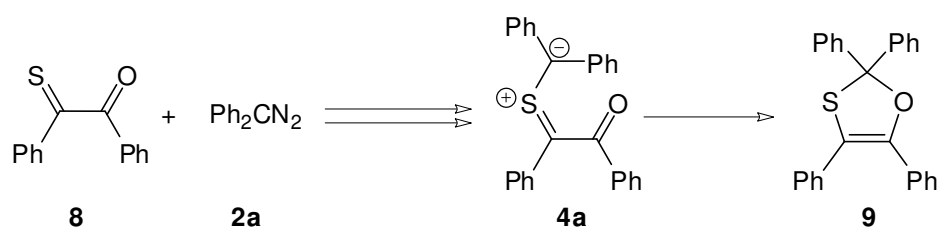
	cis-40b	40c
Crystallized from	Et ₂ O/hexane	Et ₂ O/hexane
Empirical formula	C ₂₁ H ₂₃ NS	C ₁₅ H ₁₉ NS
Formula weight [g mol ⁻¹]	321.48	245.38
Crystal color, habit	yellow, prism	red, plate
Crystal dimensions [mm]	0.10 × 0.15 × 0.17	0.03 × 0.13 × 0.13
Temperature [K]	160(1)	160(1)
Crystal system	monoclinic	monoclinic

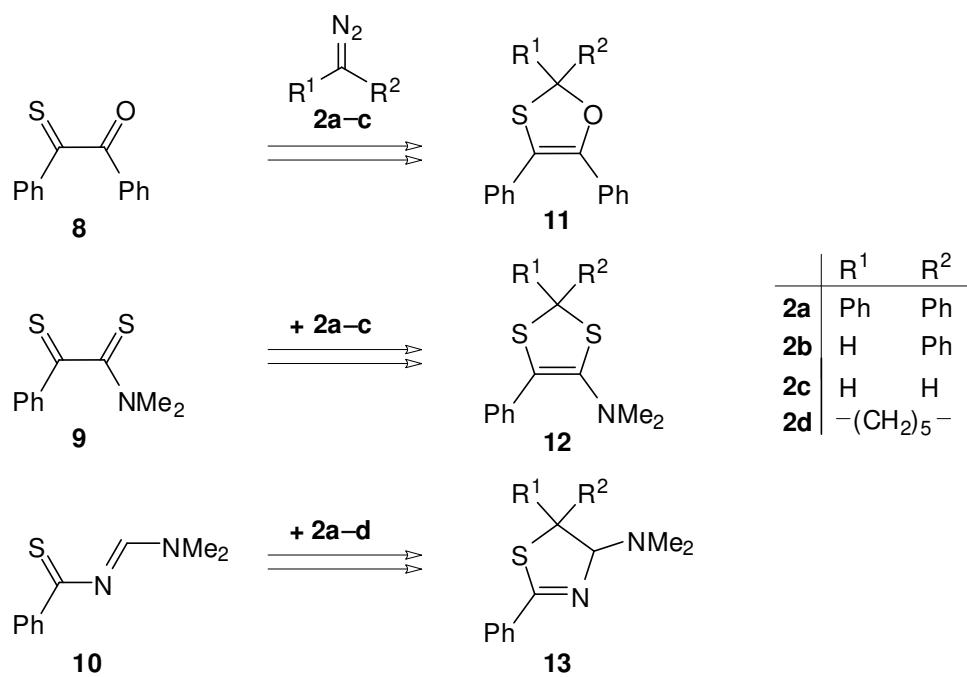
Space group	$P2_1/c$	$C2/c$
Z	4	8
Reflections for cell determination	73098	18871
2θ range for cell determination [°]	4–60	4 – 50
Unit cell parameters a [Å]	12.3385(2)	24.832(1)
b [Å]	5.9839(1)	5.1847(2)
c [Å]	23.8454(5)	21.2611(9)
α [°]	90	90
β [°]	91.564(1)	109.014(3)
γ [°]	90	90
V [Å ³]	1759.91(6)	2587.9(2)
D_x [g cm ⁻³]	1.213	1.259
$\mu(\text{MoK}\alpha)$ [mm ⁻¹]	0.183	0.227
Scan type	ϕ and ω	ϕ and ω
$2\theta(\text{max})$ [°]	60	50
Transmission factors (min; max)	0.884; 0.985	0.891; 0.996
Total reflections measured	49425	19009
Symmetry independent reflections	5157	2279
Reflections with $I > 2\sigma(I)$	3741	1623
Reflections used in refinement	5156	2278
Parameters refined	209	155
Final $R(F)$ [$I > 2\sigma(I)$ reflections]	0.0496	0.0561
$wR(F^2)$ (all data)	0.1261	0.1418
Weighting parameters (a; b) ^a :	0.0555; 0.6236	0.0577; 4.4843
Secondary extinction coeff.	0.041(3)	0.013(1)
Goodness of fit	1.046	1.097
Final $\Delta_{\text{max}}/\sigma$	0.001	0.001
$\Delta\rho(\text{max; min})$ [e Å ⁻³]	0.31; -0.25	0.31; -0.25

^a) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$

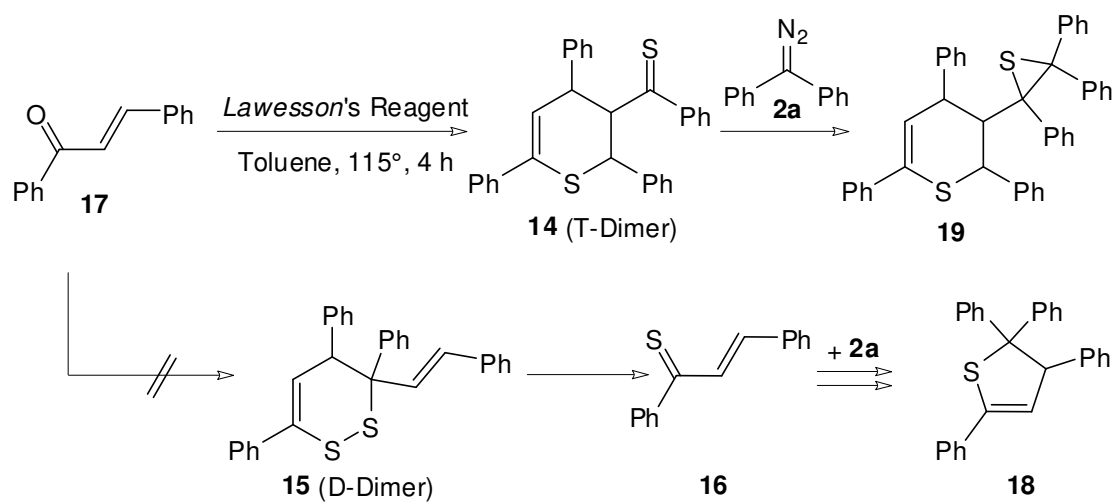


Scheme 1

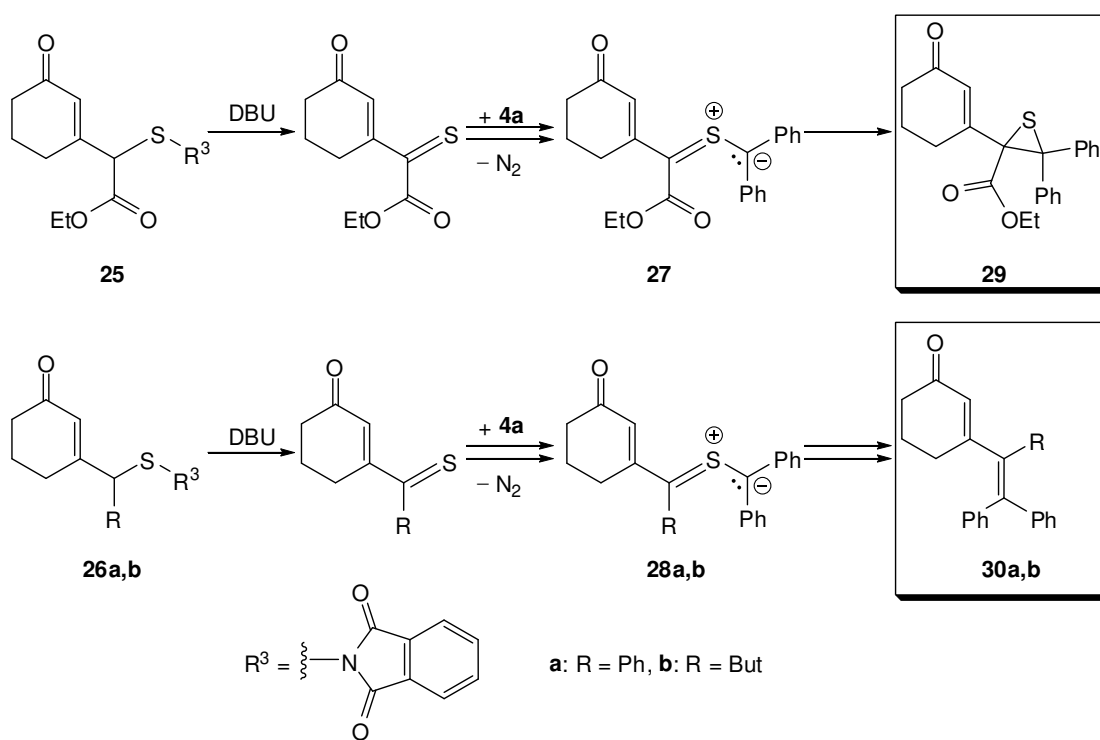
*Scheme 2*



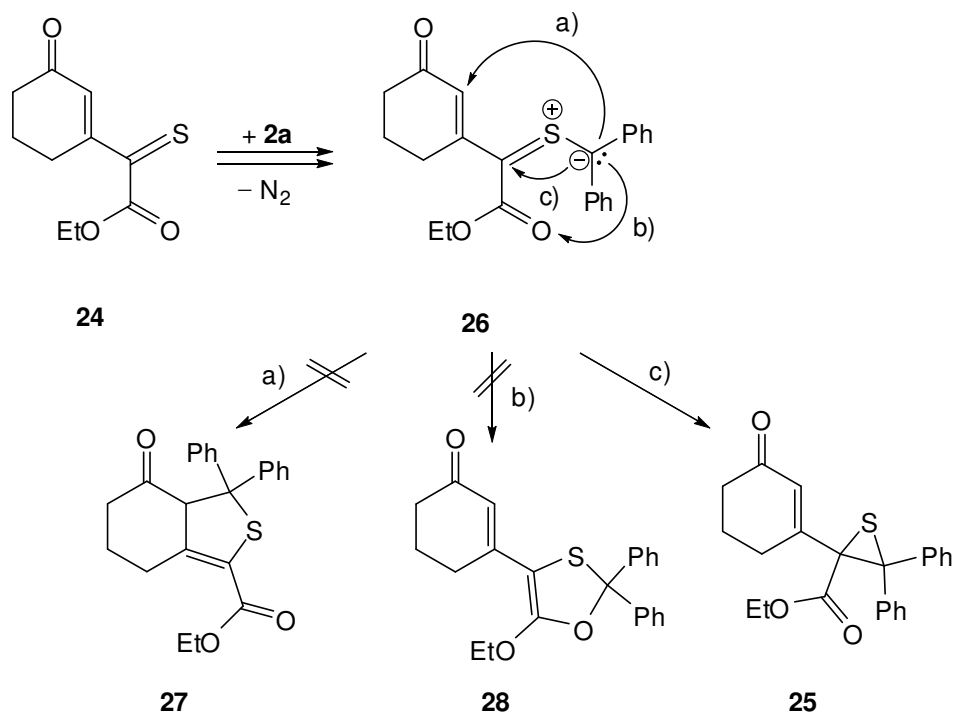
Scheme 3



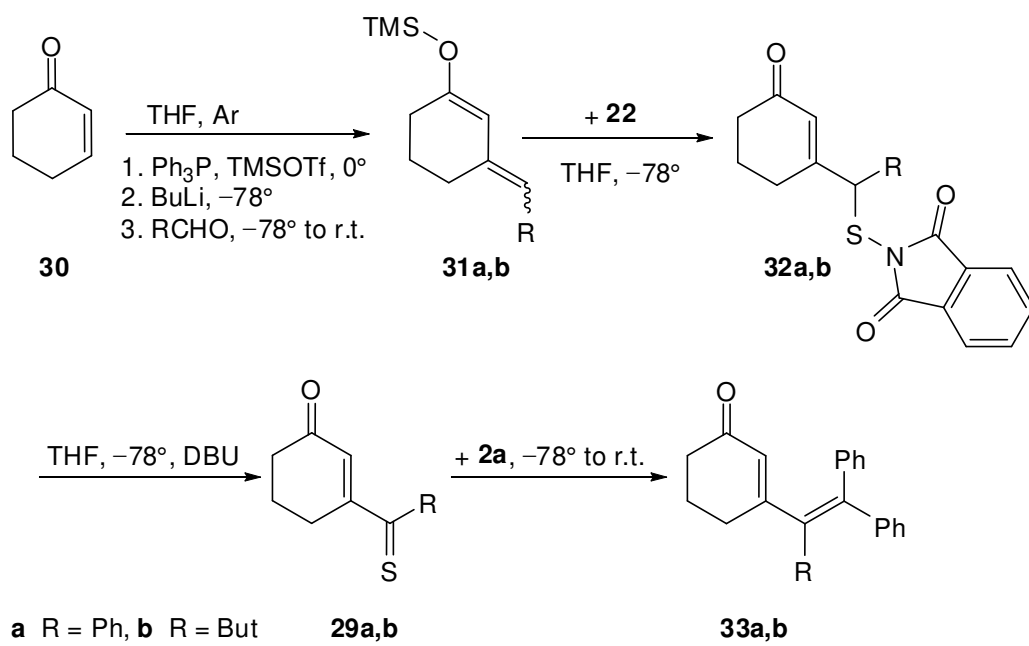
Scheme 4



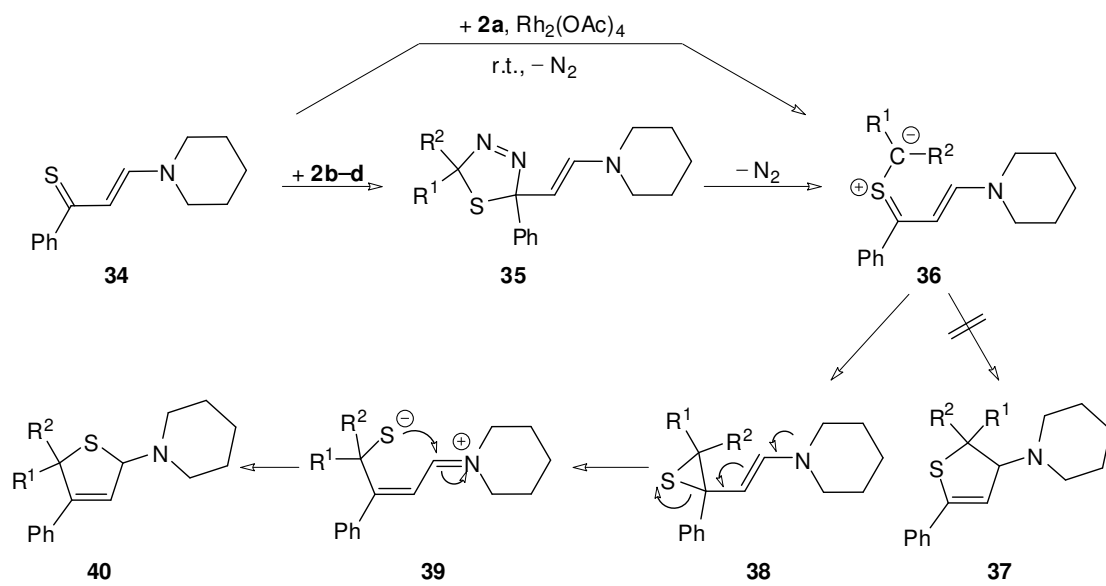
Scheme 5



Scheme 6



Scheme 7



Scheme 8

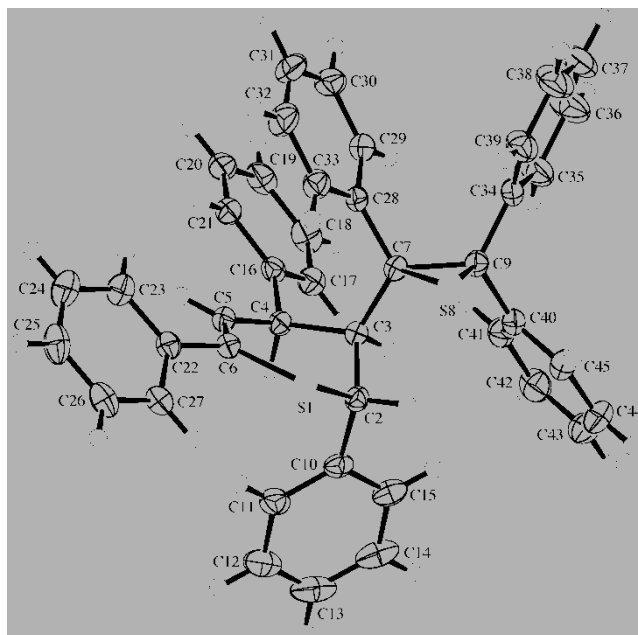


Figure 1

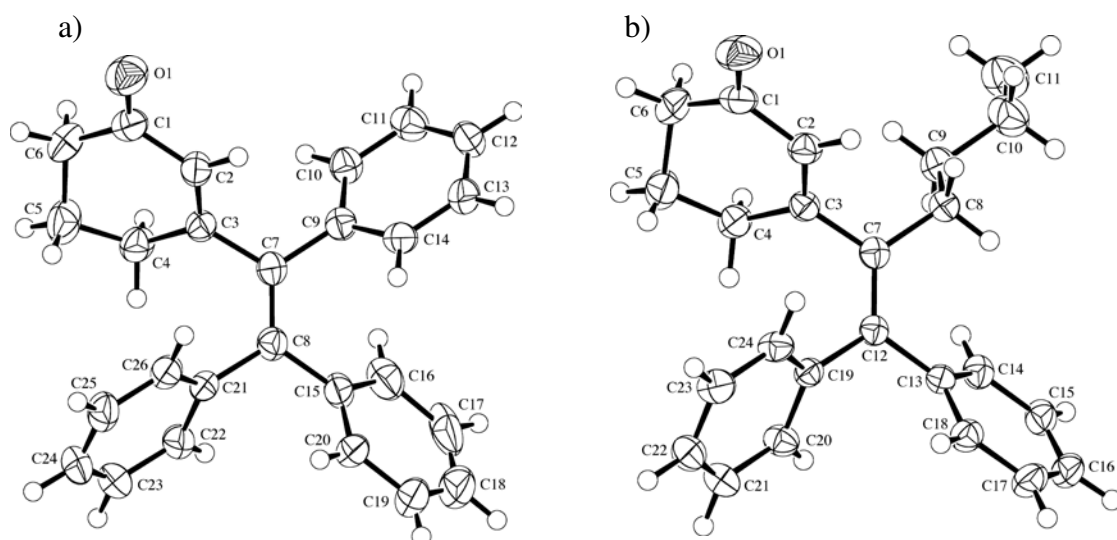


Figure 2

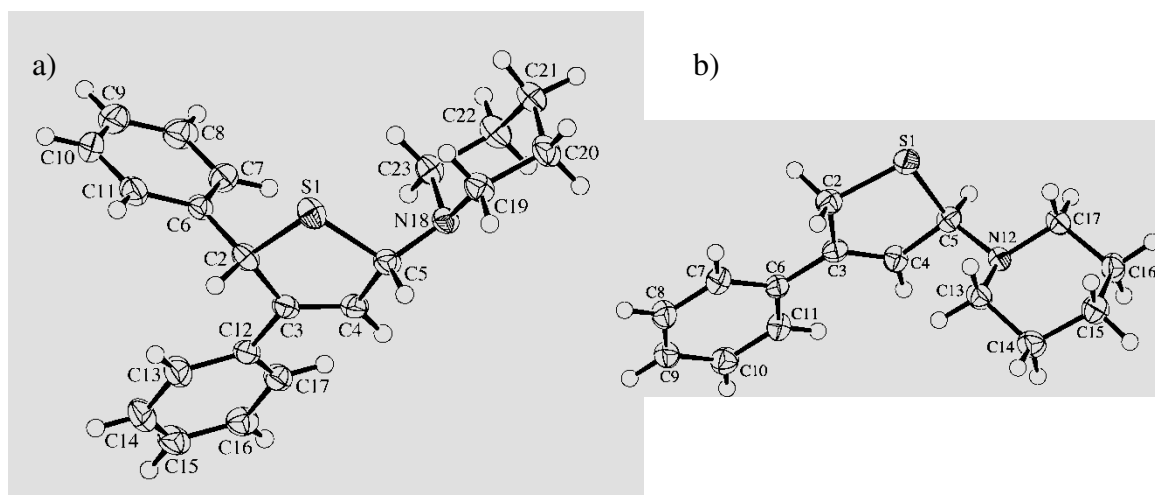
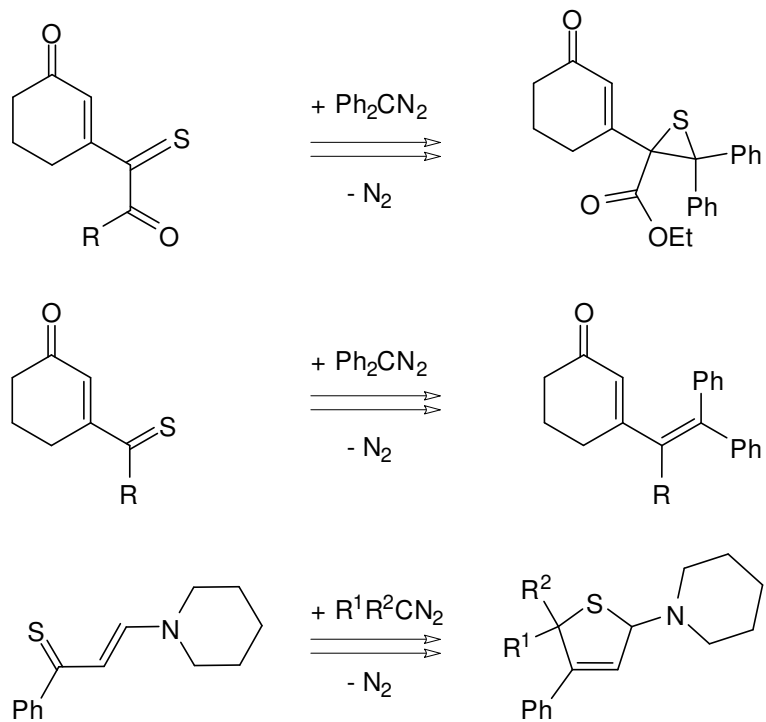


Figure 3



Chemical Abstract